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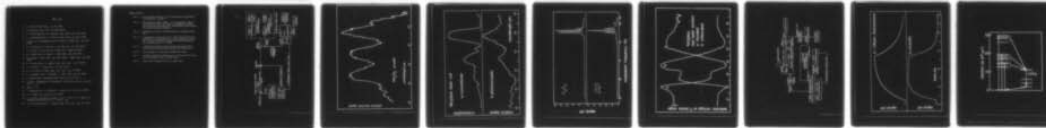
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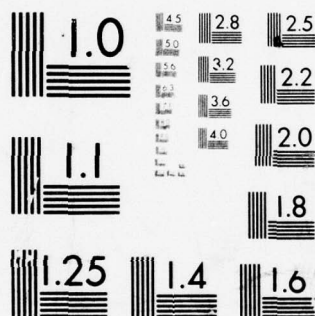
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Contract N00014-75-C-0796

Task No. NR 051-556

TECHNICAL REPORT NO. 14

PIEZOELECTRIC DETECTION OF PHOTOACOUSTIC SIGNALS

by

Michael M. Farrow, Roger K. Burnham, Max Auzanneau,
Steven L. Olsen, Neil Purdie, and Edward M. Eyring

Prepared for Publication in APPLIED OPTICS

University of Utah
Department of Chemistry
Salt Lake City, Utah 84112

September 19, 1977

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 14 TR-14	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER 9 Interim
4. TITLE (and Subtitle) PIEZOELECTRIC DETECTION OF PHOTOACOUSTIC SIGNALS		5. TYPE OF REPORT & PERIOD COVERED Technical Report, Interim
7. AUTHOR(s) 10 Michael M. Farrow, Roger K. Burnham, Max Auzanneau (Poitiers), Steven L. Olsen, Neil Purdie (Oklahoma State), and Edward M. Eyring		6. PERFORMING ORG. REPORT NUMBER 15 N00014-75-C-0796
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Utah Salt Lake City, Utah 84112		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task No. NR 051-556
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE 11 19 September 1977
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 23p.		13. NUMBER OF PAGES 20
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) piezoelectric detection fluorescence microphone photoacoustic signals radiationless decay transient response barium titanate neodymium glass transducers lasers chopping frequencies		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Piezoelectric detection of photoacoustic signals offers a number of advantages over the better known microphonic technique for condensed phase samples. Experimental techniques are greatly simplified by taking advantage of the acoustic impedance match offered by solid state detectors with solid or liquid samples. Such piezoelectric detectors prove suitable for a.c. steady state measurements as well as impulse-transient response detectors. Several example spectra of Nd(III) are presented with emphasis on the effects of the fluorescence lifetime in Nd:glass laser material.		

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ABSTRACT

Piezoelectric detection of photoacoustic signals offers a number of advantages over the better known microphonic technique for condensed phase samples. Experimental techniques are greatly simplified by taking advantage of the acoustic impedance match offered by solid state detectors with solid or liquid samples. Such piezoelectric detectors prove suitable for a.c. steady state measurements as well as impulse-transient response detectors. Several example spectra of Nd(III) are presented with emphasis on the effects of the fluorescence lifetime in Nd:glass laser material.

Introduction

There has been a recent revival of interest in photoacoustic spectroscopy or PAS, a technique invented by Alexander Graham Bell¹ in 1881, as an analytical tool for obtaining the electromagnetic absorption spectrum of both opaque and highly transparent materials.

M.M.F., R.K.B., S.L.O., and E.M.E. are with the University of Utah, Chemistry Department, Salt Lake City, Utah 84112 where this work was performed; M.A. is with the University of Poitiers, Groupe de Recherches de Chimie Physique de la Combustion, Domaine du Deffend, Mignaloux-Beauvoir, 86800 St. Julien Lars, France; N.P. is with Oklahoma State University, Chemistry Department, Stillwater, Oklahoma 74074.

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PAS of solids typically involves the irradiation of a surface in an enclosed, gas-filled cell by a chopped beam of light. If the wavelength of the monochromatic, periodic light beam entering the cell through a transparent window is one that the sample surface absorbs, the subsequent thermal deexcitation of the energy states excited by the light beam will give rise to pressure oscillations in the surrounding gas, amplitudes of which are proportional to the absorption of the light by the surface. These oscillations are detectable with a microphone also located in the cell, and the resulting signal is amplified and measured by a lock-in amplifier.²

McClelland and Kniseley³ provide a schematic of a typical microphone-PAS cell and also a plot of experimental data that suggests there is very little to be gained in Signal to Noise and nothing to be gained in photoacoustic signal by working at chopping frequencies exceeding about 50 Hz. In a subsequent note⁴ these same authors provide a clearer schematic view of how a microphone-PAS cell works and how one can overcome the disadvantage of light scattering from the sample on to the microphone by relocating the latter at the end of an interconnecting air duct. Clearly, the sensitivity of the microphone to thermal and other extraneous environmental signals mitigates against its use if some other suitable detector can be found.

In order to achieve the broad applicability associated with absorbance, fluorescence, and other analytical optical techniques, PAS must be improved in several areas, one of which is the ability to respond more rapidly to a stimulus than is possible at a 50 Hz chopping frequency. For example, Rosencwaig² demonstrated the feasibility of identifying fluorescent lines in a PAS spectrum but did not report quantitative measurements. Excepting gas phase measurements by

Robin et al.,^{5,6} for which piezoelectric detection is not the optimum choice, only a few quantitative PAS studies have been undertaken on solids of radiationless processes. Prominent among those which have been reported are studies by Callis using a piezoelectric calorimeter⁷ and cryogenic heat pulse measurements by Robin and Kuebler.⁸

Description of Method

In 1963, White⁹ demonstrated that elastic (acoustic) waves are generated in solids when an electromagnetic wave is absorbed. In 1967, Brienza and DeMaria¹⁰ showed that a mode-locked Nd:glass laser produced intense acoustic pulses in a target with a fundamental frequency fixed by the mode-locking frequency. These acoustic pulses were attributed to the absorption of energy at the optical skin depth with subsequent thermal generation of the elastic waves. In these and more recent reports,¹¹⁻¹³ the acoustic wave detector was a piezoelectric transducer. This choice is obvious given the required broad frequency response and acoustic impedance matching.

It was in fact the impedance matching argument which led us in the present work and Hordvik¹⁴ to use piezoelectric detectors for measuring the acoustic signal arising from the absorption of visible radiation in solids. The acoustic impedance, defined as the product of the density and sound propagation velocity of the medium, is analogous to electrical impedance. For most solids it ranges from 10^7 to 10^8 $\text{kg m}^{-2}\text{sec}^{-1}$ and for most liquids it is about one order of magnitude smaller.¹⁵ Most gases have much smaller impedances,¹⁵ on the order of $500 \text{ kg m}^{-2}\text{sec}^{-1}$. For an acoustic wave arriving at a boundary at normal incidence, the transmission coefficient (defined as the ratio of the

transmitted wave to that of the incident wave) is given by:¹⁶

$$\alpha_t = \frac{4R_1 R_2}{(R_1 + R_2)^2}$$

where R_1 is the acoustic impedance of the medium, i. For a typical solid-gas interface, the transmission coefficient is 3×10^{-5} . Avoiding the acoustic impedance mismatch and attaching a barium titanate transducer directly to the sample, a transmission coefficient of ~ 0.9 can be achieved, in principle. Even a liquid (water) sample in contact with a barium titanate transducer would have a transmission coefficient of ~ 0.2 .

Since as noted above the transmission coefficient for an acoustic wave at a gas-solid interface is so small, the photoacoustic signal detected by the microphone technique is not the same acoustic wave generated in the solid sample by the absorption of the incident radiation. Thus it may be misleading that the term photoacoustic spectroscopy has been applied to essentially thermal detection of the deexcitation of optically excited states as opposed to acoustic detection.

Hordvik's use¹⁴ of a piezoelectric detector operating in the 150 to 3000 Hz chopping frequency range does not capitalize on one of the principal potential advantages of such a transducer over a microphone. Kohanzadeh and Whinnery¹⁷ have reported the very broad frequency response possible when using piezoelectric detection of acoustic signals generated by the absorption of modulated low intensity laser beams. In their experiment, a liquid absorber surrounded by a cylindrical piezoelectric transducer and excited by approximately one watt of electrooptically modulated laser power showed acoustic response up to 100 kHz.

Experimental Example

Barium titanate piezoelectric transducers were used to obtain a PAS

absorption spectrum of a powdered Nd_2O_3 sample attached to a front surface mirror with Eastman 910 cyanoacrylic adhesive. In this case, the barium titanate transducer attached to the back of the mirror was an Edo-Western Corp. (Salt Lake City, Utah) EC-64 with a resonant frequency of $\sim 45\text{kHz}$. The light source was a 500 watt high pressure xenon arc lamp passed through a monochromator with $f/4$ optics and a 10 to 20 nm bandpass. The spectra have been source compensated, i.e. normalized for differences in lamp intensity at different wavelengths. The signal was received with a Princeton Applied Research Corporation (PARC) Model 184 charge amplifier and Model 124A lock-in amplifier. The light beam was chopped mechanically at a frequency of 135 Hz, and the output signal level was in the range of 100 to 200 μV . A block diagram of this photoacoustic spectrometer is shown in Fig. 1. The point of primary interest to Fig. 2 is that it is almost trivially easy to obtain the highly detailed visible light absorbance spectrum of neodymium(III) oxide from a completely opaque, solid sample using the above described PAS spectrometer.

In Fig. 3 we have compared the PAS spectrum of an essentially transparent neodymium(III) glass laser rod (Owens-Illinois) with the absorbance spectrum of the same material obtained with a Beckman DB uv-visible spectrophotometer digitized with a Digital Equipment Corp. LSI-11 microcomputer. The PAS experiment was performed with the laser glass ($\sim 2\text{cm}$ thick) mounted on a first surface mirror backed by a barium titanate transducer as in the experiment of Fig. 2. All other features of the experiment were as described above. The 10 to 20 nm bandpass of the monochromator was imposed by arc wander in the light source (that had been minimized by a permanent magnet). Both the front surface mirror and adhesive were used in these experiments as they show minimal optical absorption in the wavelength range reported. In the case of an opaque

material that does not bleach, the use of a mirror might be considered redundant since its function is to prevent any scattered light from illuminating the transducer since such illumination would lead to spurious detector response.

Much higher chopping frequencies can be used with piezoelectric detection since the acoustic signal is attenuated less in passing through a solid than through a gas. In order to demonstrate this, we modulated the output beam from a Spectra Physics argon-ion laser with an Isomet model 1206 acousto-optic modulator and used the first order diffracted light, which is modulated to a 100% depth, to excite a flat black painted portion of the front surface mirror with transducer attached as described above. Figure 4 shows the detected signal for the range 10 Hz to 200 kHz (upper frequency limit of the lock-in amplifier) for both sinusoidal and square wave modulation. In both cases the average power incident on the sample was ~ 190 mW at $\lambda = 488$ nm. It should be noted from the vertical scale of Fig. 4 that the acoustic signal level is greater for square wave modulation in accordance with the calculations of R. M. White⁹. The very strong signal level near 40 kHz is attributable to the response at the resonance frequency of the piezoelectric and suggests the possibility of enhanced sensitivity achievable by modulating at or near the resonance frequency of the transducer.

The linear response of a piezoelectric transducer over a broad frequency range up to the resonant frequency allows the optimum chopping frequency to be chosen for a particular system, or a range of chopping frequencies to be used to obtain kinetic information. The lack of symmetry of the peaks in Fig. 4 occurring near resonance for the sinusoidally modulated experiment is attributable to the choice of frequencies sampled and not to the nature of the piezoelectric transducer.

Impulse response is often less difficult to analyze than the steady state response. For example, Fig. 5 shows the steady state PAS response of a Nd:glass

sample to the mechanically chopped, high intensity output of an argon ion pumped, Rhodamine 6G CW dye laser. In this case the Nd:glass sample was a 2 cm diameter rod 5 cm in length. The transducer was mounted on an aluminum saddle glued to the side of the rod near the front face such that the plane of the transducer was parallel to the long axis of the rod. Illumination was along this long axis. In no case was any of the exciting radiation scattered from the optical quality laser rod onto the transducer or its aluminum mount. An unexpected result was a phase shift in excess of 180° , dependent on the radiation density of the excitation at the sample.

When the dye laser beam was focused to a ~ 0.1 mm spot diameter, the detected acoustic signal (voltage) as a function of excitation wavelength first increased and then went negative as the optical absorption band centering on 588 nm was traversed. This was not observed if the dye laser beam was defocused so that the entire sample surface was illuminated. This effect we tentatively attribute to a ground state depletion, which could produce anomalous phase shifts by distortion of the acoustic waveform. Indeed the acoustic waveform was noticeably distorted relative to the excitation function when observed on an oscilloscope. In light of these difficulties and recalling Callis' success using a piezoelectric calorimeter,⁷ we proceeded to test the acoustic response of a Nd:glass sample to square wave impulse excitation.

The Callis piezoelectric calorimeter restrained a sample and piezoelectric transducer in a rigid frame so that any thermal expansion of the sample compressed the piezoelectric material and produced an electrical impulse.⁷ For our experiment we used the mirror-transducer assembly used to produce Fig. 4 with a cylindrical Nd:glass sample (2 cm diameter, 2 cm in length) attached with cyanoacrylic adhesive. As noted above, this assembly has flat response up to ~ 40 kHz

(Fig. 4) and this bandwidth can reproduce undistorted impulse responses with rise-times as short as ~ 10 μ sec. This configuration will respond to acoustic waves but to thermal effects only when the transducer itself is heated. This is unlike the Callis piezoelectric calorimeter which compresses the transducer when the sample expands.⁷ Figure 6 is a block diagram of the transient response system. The excitation beam from an argon ion laser operating at 514.4 nm was pulse modulated with an acousto-optic modulator of local design and manufacture. The optical pulse diffracted by the modulator was selected with an iris and focused with a lens on the sample. The sample geometry was arranged such that any fluorescence emerging from the sample would pass through a CS2-58 Corning glass filter (to eliminate 514.5 nm radiation and pass the fluorescence at wavelengths longer than 700 nm) and through a Bausch and Lomb 33-86-40 monochromator and detected with an S1 response photomultiplier (with a risetime shorter than 1 μ sec). With this arrangement, either the acoustic signal or the fluorescence signal could be monitored. In both cases a PARC model 183 photometric preamplifier was used and the unfiltered signal available at the "Monitor" port was detected and digitized by a Tektronix R7912 Transient Digitizer. The Transient Digitizer was controlled by a PDP 11/10 minicomputer (Digital Equipment Corp.), operated with Tektronix Waveform Enhancement Software (W.E.S.). Since individual acoustic transients had a very low signal to noise level and since the W.E.S. operating system is limited in its computational capability, an LSI-11 microcomputer (Digital Equipment Corp.) was used to receive the individual processed and digitized wave forms (512 data points) from the R7912-PDP 11/10 system. These were added together timewise until enough transients in a computer of averaged transients (CAT) technique were collected to raise the signal to noise ratio to an acceptable level.

The excitation pulses were of 1 msec duration with rise and fall times of 0.5 μ sec, fixed by the acousto-optic modulator. The PARC preamp had measured rise times of $\sim 6 \mu$ sec on 10^{-8} A/V amplification used for the acoustic signal and 3.5 μ sec for 10^{-7} A/V amplification used for the fluorescence signal. Figure 7 shows the cumulative result of summing 1000 transients in the CAT for the acoustic signal and 100 transients for the fluorescence at 1060 nm, with a total time window of 2 ms depicted.

Although analysis of the complete system will not be presented here, features of the impulse response measurements are noteworthy. It is apparent that the acoustic response differs from the optical response in that the acoustic risetime is measured to be $\sim 540 \mu$ sec (bandwidth at 3dB less than 1 kHz) whereas the optical risetime was $\sim 670 \mu$ sec. In a glass host, Nd^{3+} is a four electronic level system (Fig. 8) with absorption followed by a fast (nanosecond) radiationless decay to the triplet state. The triplet decays by fluorescence with a lifetime of tens to hundreds of microseconds, determined by host material and dopant concentration.¹⁸ The fluorescent terminal state is about 2000 cm^{-1} above the ground state and is known to decay rapidly (nanoseconds) through a radiationless process to the ground state. Our tentative explanation for the fact that the observed acoustic time constant is fast compared to the optical time constant is that intersystem crossing and radiationless decay is rapid compared to the fluorescence lifetime. (The acoustic time constant is undoubtedly limited by the bandwidth of the transducer). The absence of an acoustic response corresponding to the smaller radiationless decay from the fluorescent terminal state to the ground state is attributed to a lack of sensitivity. It is clear from the differences in the two risetimes that the acoustic response is not dependent on the optical response.

Conclusion

The use of piezoelectric detectors for measuring optically generated acoustic signals in condensed phases offers greater versatility than microphonic techniques. Sensitivity similar to that attained with microphones is possible, but without the physical vulnerability of a microphone. Piezoelectric transducers are made that can operate from 4°K to 700°K ,⁷ and with frequency response as high as hundreds of megahertz.¹⁹ Piezoelectric transducers can perform satisfactorily in either an a.c. mode or an impulse mode offering additional freedom to the experimenter. Furthermore, the feasibility of detecting only the acoustic wave rather than its thermal effects permits direct analysis of phase angle relationships and facilitates identification of the signal source. In particular, we foresee the use of this technique in measuring lifetimes of dark (radiationless decay) processes in opaque materials on nanosecond time scales. Indeed, Von Gutfeld and Melcher²⁰ have recently demonstrated 20 MHz acoustic response from 5-10 nsec laser pulses; this corresponds to an ~ 8 nsec rise time.

Acknowledgements

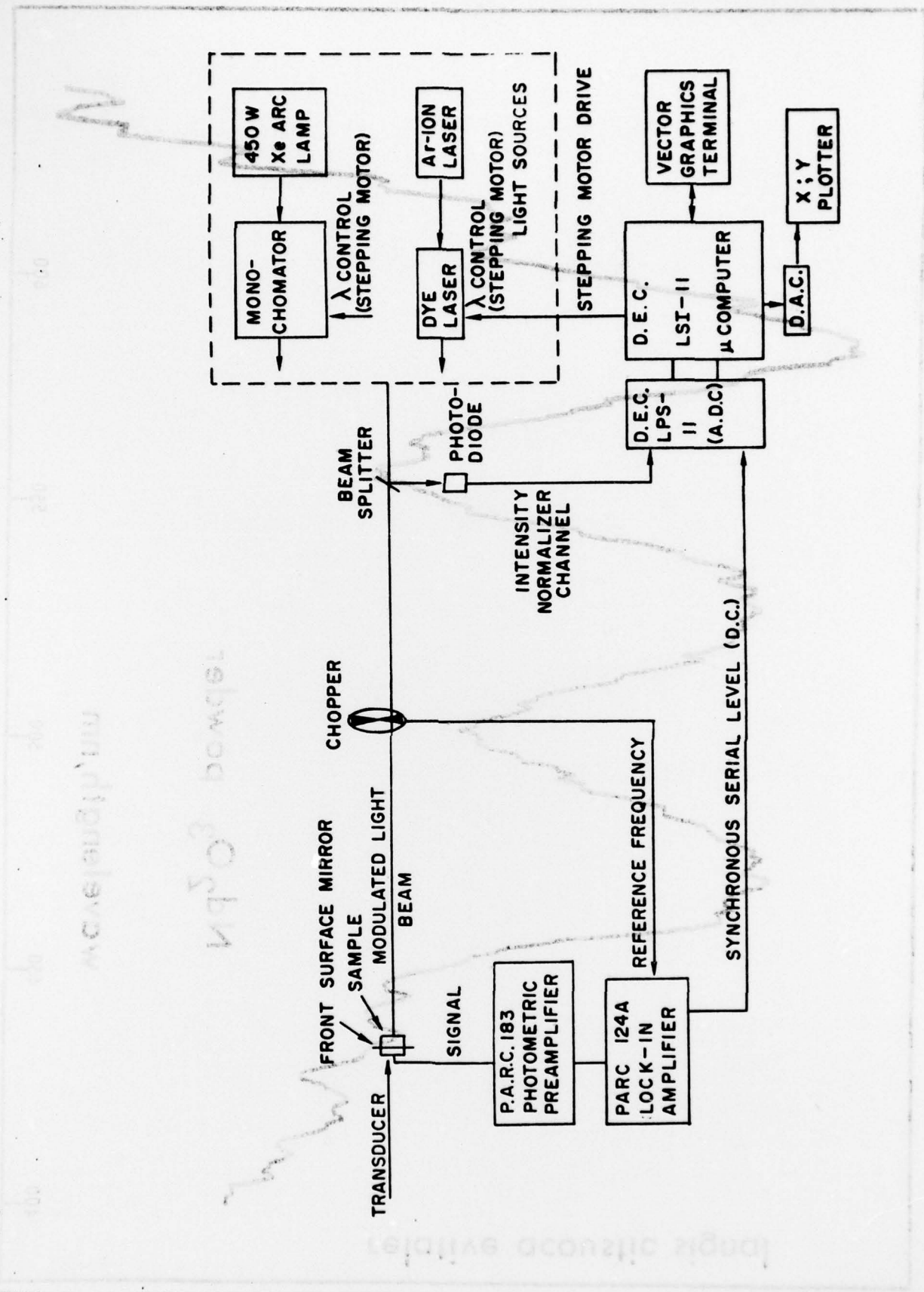
This research was supported by AFOSR Grant 77-3255 from the Chemical Directorate of the Air Force Office of Scientific Research, by an Office of Naval Research contract, and by Biomedical Research Support Grant RR-07092 from the General Research Support Branch, National Institutes of Health. Advice and assistance from Professor Joel M. Harris and from Paul Malnati of Tektronix, Inc. is also gratefully acknowledged.

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Figure Captions:

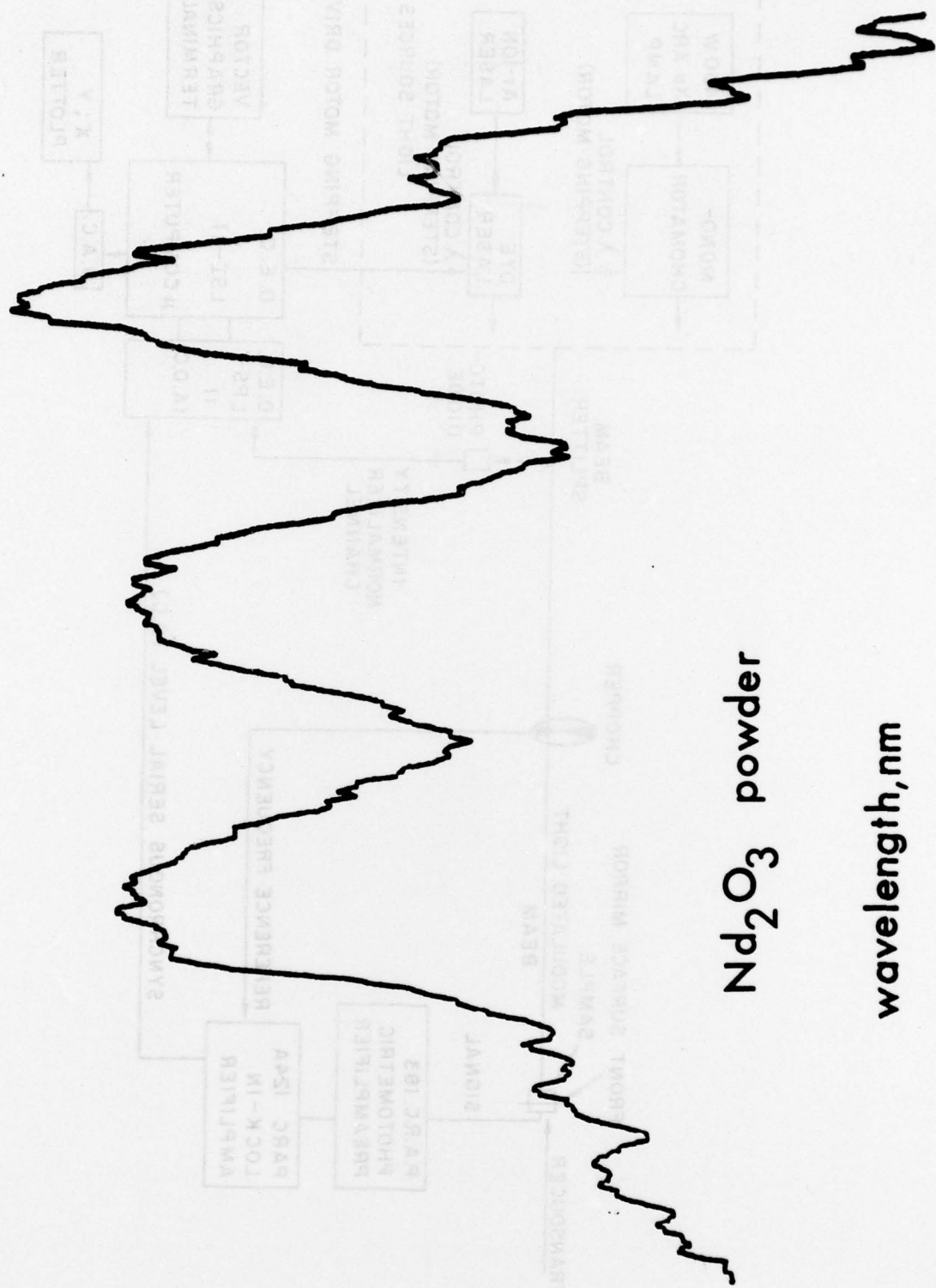
- Fig. 1. Block diagram of photoacoustic spectrometer incorporating a piezoelectric transducer.
- Fig. 2. PAS spectrum of Nd_2O_3 powder. To avoid spurious signals from scattered light, the sample is imbedded in a cyanoacrylate matrix and placed on a front surface mirror backed by a barium titanate transducer.
- Fig. 3. Comparison of optical and PAS spectra of a Nd:glass laser rod.
- Fig. 4. A comparison of the response of a flat black paint-mirror-piezoelectric transducer system to both squarewave (lower) and sinusoidally modulated (upper) excitation at 488 nm and an average power of ~ 190 mW.
- Fig. 5. A comparison of PAS spectra of Nd:glass obtained with a focused and unfocused, modulated dye laser light source.
- Fig. 6. Block diagram of a transient response PAS system.
- Fig. 7. Transient response of Nd:glass to a 1 ms pulse at 514.5 nm: (a) Fluorescence signal; (b) PAS signal.
- Fig. 8. Energy level diagram of Nd^{3+} in a glass host.

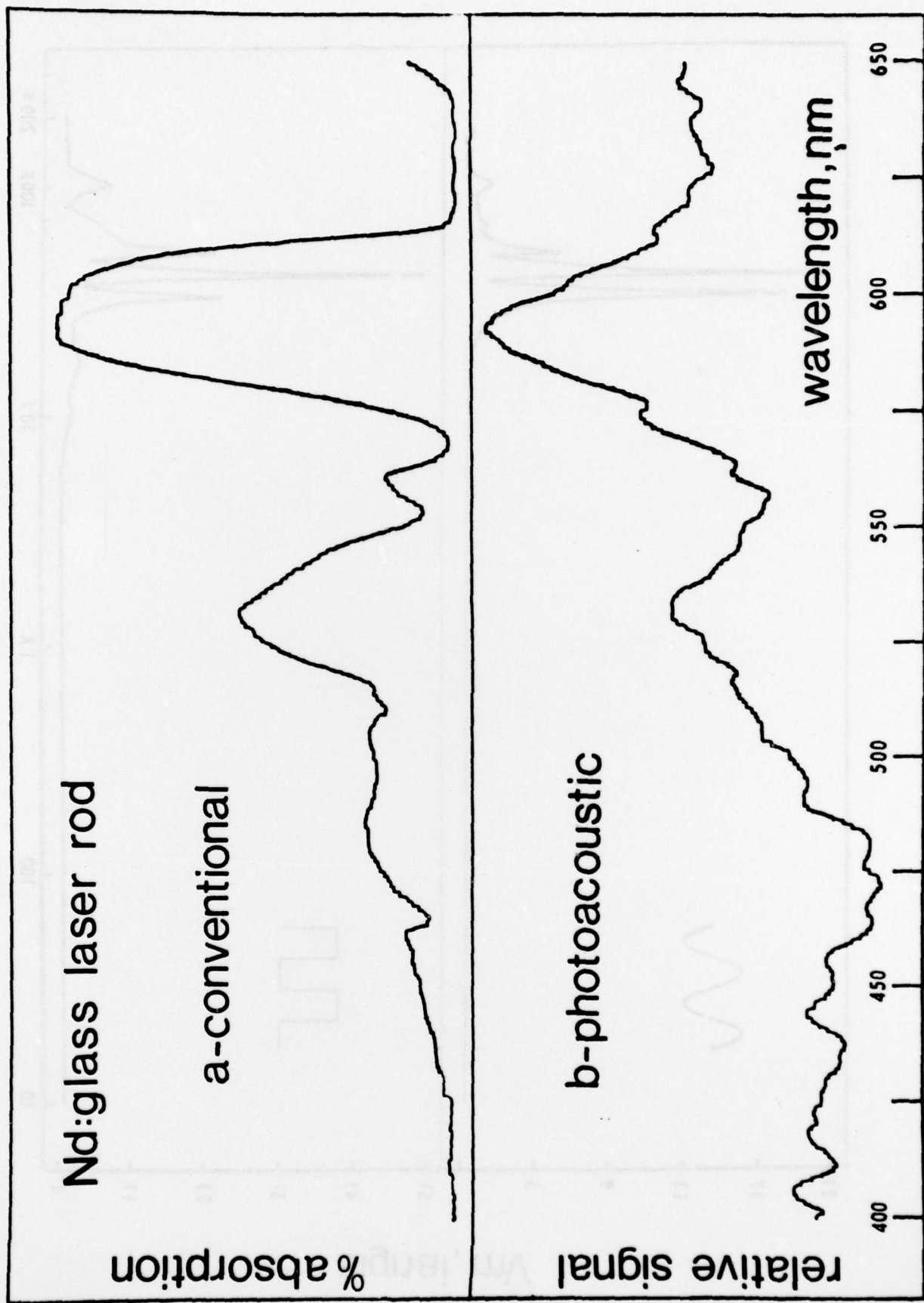


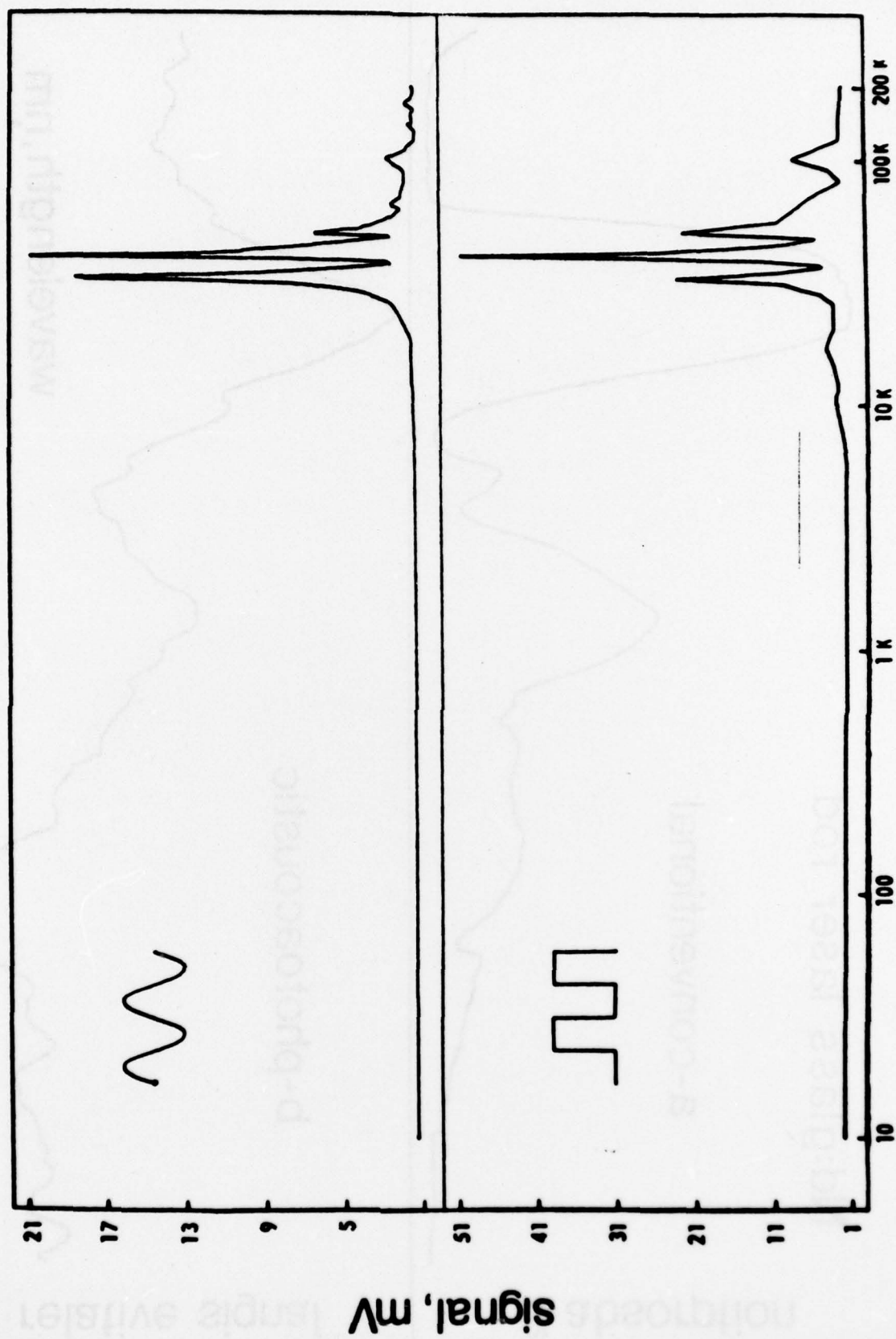
relative acoustic signal

Nd_2O_3 powder

wavelength, nm







modulation frequency, Hz

